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Report 166-F

**CHARACTERIZATION OF CERTAIN
POLYMERIC MATERIALS**

Jet Propulsion Laboratory
California Institute of Technology
Purchase Order AM4-226583
Prime Contract NAS 7-100
January 1964

ASTROPOWER LABORATORIES

2121 PAULARINO AVE. NEWPORT BEACH, CALIFORNIA

MISSILE & SPACE SYSTEMS DIVISION
DOUGLAS AIRCRAFT COMPANY, INC.
SANTA MONICA, CALIFORNIA

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1.0 INTRODUCTION

Dicyanoacetylene (DCA) has been known for over 40 years and has been scantily investigated during that time. The most thorough research into its preparation, characterization and reactions was that of Moureu and Bongrand (Reference 1). Subsequent to their work, other investigators examined the reactions, combustion, and spectral properties of DCA, but in each instance the method of preparation was almost identical to that described in Reference 1. Recently, the polymerization characteristics of DCA were examined in some detail with the intent of obtaining a polymer capable of being an organic semiconductor (Reference 2) but with more definite properties than the "black Orlon" reported from the pyrolysis of polyacrylonitrile. However, only anionic polymerizations were studied and no mention has been made in the literature about the free radical polymerizability of DCA. Our interest centered around the copolymerization characteristics of DCA with other monomers, by whatever means would present itself - anionic or free radical. It was our intention to obtain homopolymer and copolymers which would have a fairly high molecular weight and have some degree of conductivity. In addition, we would be interested in obtaining the reactivity ratio of a particular copolymer, if possible. With these goals in mind, we embarked upon a program of synthesis, polymerization and characterization during the eight months of the contract with the hope of ultimately obtaining a new and useful organic semiconductor.

2.0 SUMMARY

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Dicyanoacetylene monomer was prepared in 40% yield through the dehydration of acetylenedicarboxamide. The reported melting point for the diamide was found to be in error by 100°C. Other methods for preparation of the dinitrile, e.g., cyanogen bromide reaction with dilithium acetylide, were not successful. The monomer was homopolymerized and copolymerized with both anionic and free radical initiation. The free radical polymerization was the first such reported for dicyanoacetylene. The copolymerization was effected with styrene as the comonomer and it was observed that the rate of polymerization to high conversion was extremely slow when polymerized alone, but increased rapidly when styrene was present in appreciable amount. An explanation is put forward to clarify the results. Attempts at determining the r_1 and r_2 values by chemical analysis were difficult because of the poor results obtained from the elemental analysis. However, by means of the infrared spectra for the copolymers the r_1 (styrene) was found to be 1.40 and r_2 (DCA) to be approximately zero. Softening points for the polymers were obtained as well as a rough approximation of the conductivity. Attempted determination of the molecular weight led to questionable results although it did seem to consistently fall somewhere in the general region of 200 to 400. *Author*

3.0 EXPERIMENTAL*

3.1 Acetylenedicarboxamide (I)

The method used was a slight modification of that reported by Blomquist and Winslow (Reference 3) and by Moureu and Bongrand (Reference 1).

To 80 ml concentrated NH_4OH , dissolved in 100 ml ethanol and cooled to -19°C , was added 20 g of acetylenedicarboxylic acid dimethylester (Gallard-Schlesinger Chemical Mfg. Co.) dissolved in 100 ml of ethanol. The addition was dropwise with vigorous stirring and the temperature was maintained around -14°C . Upon completion of the addition, the temperature was allowed to rise to $+15^\circ\text{C}$ and the slurry filtered, washed with water until washings were neutral to pH paper, and finally washed with alcohol. The powder was dried in a vacuum desiccator for 24 hours yielding 13 g (83%) of I, melting point 195°C (dec.). (Reported mp. $290-292^\circ\text{C}$. (Reference 3))

Anal. Calc'd. for $\text{C}_4\text{H}_4\text{N}_2\text{O}_2$: C, 42.85%; H, 3.59%; N, 24.98%

Found: C, 42.86%; H, 3.75%; N, 25.04%

3.2 Acetylenedicarbonitrile (DCA) (II)

A modification of the Moureu and Bongrand procedure was used (Reference 1). A mixture of 100 g of washed and ignited sand, 50 g P_2O_5 and 6 g of acetylenedicarboxamide (I) was prepared in a 1000 ml long-neck, round bottom flask. At the end of the neck, near the standard taper joint, was placed a plug of glass wool and the flask attached to a rotating evaporator (Rinco-Vac). The take-off from the evaporator was attached with rubber tubing to a vacuum system as shown in Figure 1.

The entire system was evacuated to 10 microns and a bath, heated to 215°C , was brought into sudden contact with the rotating flask containing the reactants. At the same time, the first receiver and the trap were immersed in liquid nitrogen. Within a minute after immersion in the bath, the product began to collect in the first receiver and the pressure began to rise in the system. The reaction was allowed to continue until the pressure dropped to about 30 microns, usually about 30 minutes. At this point, the heat was removed and the flask and pump were isolated from the system by closing the two stopcocks.

*Elemental Analyses by Elek Micronalytical Laboratories, Los Angeles 16, Calif. All melting points are uncorrected.

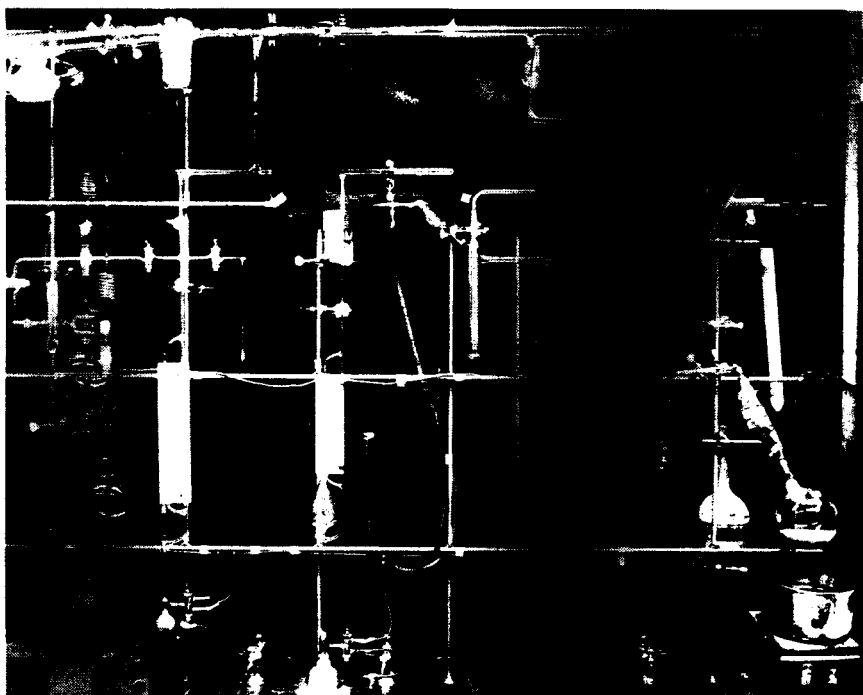


Figure 1. Setup for Monomer Preparation

The liquid nitrogen was removed from the trap and the first receiver, and placed around the ampoul. The white crystalline material was now distilled into the ampoul. When all collected, the system was evacuated to 10 microns and the ampoul sealed off. The yield was 1.65 g, 40.7%.

3.3 Polymerization and Copolymerization of DCA (II)

3.3.1 Free Radical Method

The following is representative of the many radical-catalyzed polymerizations performed.

A high vacuum rack as shown in Figure 2 was used and the following items attached:

- a. A storage reservoir for the tetrahydrofuran (THF)
- b. A secondary reservoir for THF
- c. Various ports for the attachment of graduated receivers and tubes for distilling and receiving the monomers and solvent.

Into a 25 ml capacity polymerization tube, was placed 31 mg of azo-bis-isobutyronitrile (E. I. du Pont de Nemours & Co.). This was attached to the vacuum rack and 3 ml of DCA was distilled into it under vacuum. To this was added 6 ml of THF, which had been stored over Na-K alloy under vacuum, and 3 ml of styrene monomer, each distilled in separately under vacuum. The polymerization tube was evacuated to 1×10^{-5} mm Hg and sealed off. It was placed in a 55°C oven for 21 hours and when removed there was found to be a clear, deep brown solution. The ampoul was opened and the solvent removed under a stream of nitrogen to recover 5.27 g (97% yield) of a dark gray powder.

Other polymerizations involved different volumes of monomers and were carried out for different periods of time, but they all were prepared in a similar manner as described above.

3.3.2 Anionic-Initiated Copolymerization

A polymerization tube, into which had been placed a magnetic stirring bar and which contained a short side arm, was attached to the vacuum rack. The side arm was capped with a self-sealing serum bottle cap,

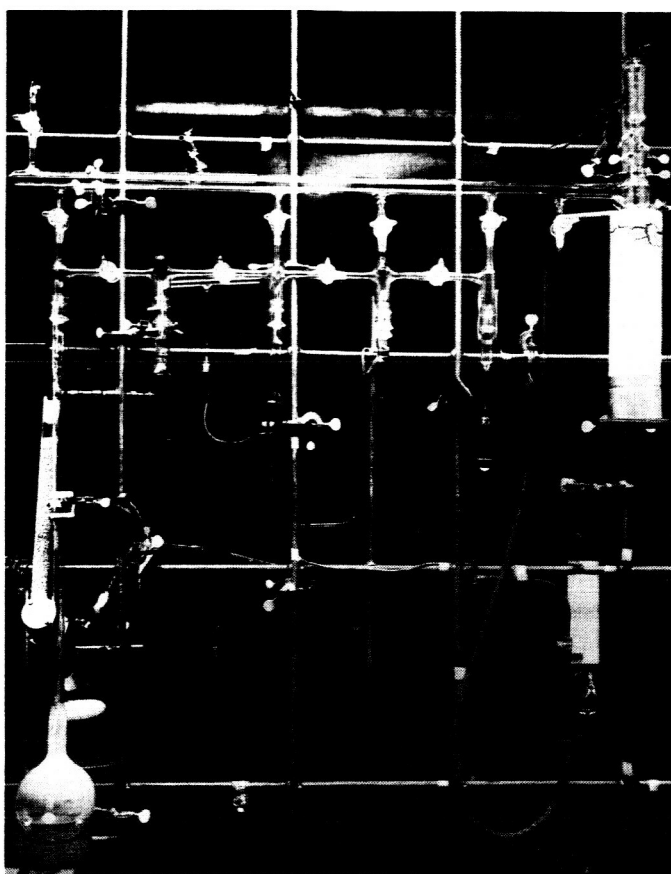


Figure 2. Setup for Polymer Preparation

and while a positive pressure of N_2 was maintained in the tube there was injected 0.05 ml of a 15% solution of n-butyl lithium in hexane. The tube was cooled with liquid nitrogen and evacuated to 10^{-5} mm Hg. The sidearm was sealed off and 3 ml of toluene plus 1.5 ml of styrene were distilled into the tube. The entire system was still being kept under liquid nitrogen. At this point, the liquid nitrogen was replaced with a dry ice - CCl_4 -acetone bath which was designed to keep the system at $-30^{\circ}C$. After 1-1/2 hours at this temperature, the solution appeared to be getting slightly viscous (as determined by the stirring bar's action under the influence of a magnetic stirrer), and 0.3 ml of DCA was distilled into the tube. Immediately, a deep brown solution developed and a small amount of blackish material deposited on the walls. Up to this point, the stirring had not been necessary and was only done intermittently. Now, it became difficult to maintain both the stirring action and a constant temperature. Thus, the temperature began to fluctuate between $-30^{\circ}C$ and $+10^{\circ}C$, staying mostly around $-20^{\circ}C$. About 1-1/2 hours after the first DCA addition, another 0.5 ml was added. No change in viscosity was noticed. After 45 minutes more another 0.4 ml of DCA was added; there seemed to be no further indication of polymerization. Where before, the addition of the DCA had resulted in an immediate darkening of color or separation of black solid, now the entering material deposited as white crystals on the upper walls of the tube and this would drop into the reaction mixture and gradually dissolve. Forty-five minutes later another 0.35 ml of DCA was added and one hour after this the remaining 0.25 ml was added. The mixture was kept at $-48^{\circ}C$, for 12 hours and then opened to the air. A few ml of methanol were added along with a few crystals of hydroquinone. A deposit appeared to be on the bottom of the tube. This solid, when filtered from the solution yielded 0.177 g of black material. The filtrate upon evaporation, yielded 0.368 g of a dark brown solid.

3.4 Extraction of Polymer

A representative extraction consisted of placing 3.7728 g of polymer into a soxhlet thimble and extracting with water for about 48 hours. This was followed by methanol for 48 hours, toluene for 43 hours and finally with acetone for 21 hours. The various solvents were evaporated in order to obtain the fraction of material soluble in each solvent. The total material balance gave a recovery value of 3.7660 g (0.0068 g loss in handling).

4.0 DISCUSSION AND RESULTS

4.1 Preparation of Dicyanoacetylene

It had been established early in the program that the preparation and polymerization of dicyanoacetylene (DCA) to a high molecular weight polymer or copolymer was the most important aspect of the program. Subsequent measurements relating to the copolymerization ratios (r_1 , r_2), molecular weights and conductivity data would follow accordingly. However, as was quickly found, the problems relating to the preparation of the monomer were manifold, and without a good source for the monomer the program would reach a stalemate. Up to the present, the only source for the monomer is the method described originally by Moureu and Bongrand (Reference 1) and subsequently by Blomquist and Winslow (Reference 3), and the yield, at best, was 37%. In order for us to utilize large quantities of DCA for the number of polymerizations contemplated, we would have to have had a better yield than this or limit the scope of the program.

In view of the great difficulties relative to the preparation of DCA monomer as reported in the literature and experimentally encountered by us, it was decided early in the program to expend a reasonably large amount of effort towards the synthesis of II. Moureu and Bongrand recognized the numerous difficulties involved and pointedly stated that the preparation of the dinitrile is a delicate operation which may give either a poor or a satisfactory yield depending upon the manner in which the reaction is conducted (Reference 1). In addition, work performed at Aerospace Corp. by H. H. Takimoto, et al, (Reference 4) further pointed up the difficulties with regard to the preparation of the diamide (I) and the DCA (II). They obtained poor yields of II and apparently considered the method inadequate. Consequently, they sought out alternative approaches with no success. Dr. A. Rembaum of JPL was also cognizant of the poor yields reported and believed that unless a ready source of the monomer was found, the efforts required for the subsequent polymerization studies would be slowed (Reference 5). Accordingly, a two-pronged attempt was made to prepare the DCA. On the one hand, a study was undertaken utilizing the method of Moureu and Bongrand as a basic approach; on the other, alternative methods were investigated.

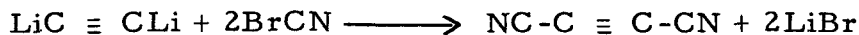
One of the first difficulties encountered was the consistent 100°C discrepancy which existed between the reported melting point of the diamide

and what we found. An analysis of the product, however, showed us to have the correct material and that the literature's error may have been typographical. Next, proceeding according to the method outlined in Reference 3 for the preparation of the dinitrile, excepting that a vacuum of 1×10^{-5} mm Hg was used in place of the stream of CO_2 at 2 mm Hg pressure, there resulted a very poor yield of DCA. It soon appeared quite obvious that one of the reasons for the poor yield was the fact that the dehydration of the diamide to the dinitrile was a solid phase, unstirrable reaction, and the resulting product, DCA, could not get out of the reaction zone rapidly enough to prevent it from decomposing or polymerizing. With the advent of the rotating evaporator (not available at the time of the Blomquist and Winslow work (Reference 3)), it seemed to present a possible approach to minimizing the difficulties encountered in heterogeneous solid phase reactions. With this instrument one could have thorough mixing as well as a continuously moving surface thereby preventing the trapping of any product. Utilizing a rotating evaporator (Rinco-vac) and a 1-liter, long neck flask as a reaction vessel, we were ultimately able to obtain a 40.7% yield of DCA with excellent reproducibility. The only difficulty was the fact that here, too, an unmovable solid phase developed. Apparently, as soon as the reaction mixture was heated, it began to cake, and no matter how long it was rotated it did not crumble - even with a few glazed stones in the flask. Another problem was the matter of stability of the isolated DCA. Even though prepared and sealed off under high vacuum, and stored in a freezer, a progressive decomposition resulted, as evidenced by the formation of a brown color in the ampoul. This decomposition had been observed elsewhere (References 6 and 7), and the suspected agents causing the decomposition were oxygen and light.

Therefore, this posed problems with regard to the availability of the monomer for polymerization purposes. Although the yields were consistent, they were low. This meant expending a large effort towards preparing enough batches of monomer for the number of polymerizations necessary, or to seek out an alternative synthesis which would allow us to prepare large batches of DCA from which we could draw as needed. Thus, about 20% of the original six month program was devoted to another synthesis of DCA.

The preparation of metal acetylides, and, in particular, the alkali metal acetylides, and their subsequent reactions with various materials such

as carbon dioxide, ethylene oxide, and other compounds, is well known. In view of the ready availability of dilithium acetylide from the Foote Mineral Co., it seemed quite likely that this material, plus cyanogen bromide, might give DCA in a simple one-step reaction.



Unfortunately, although the reaction might proceed as shown, before all the cyanogen bromide has had a chance to react, any DCA which does form is still in the presence of the dilithium acetylide, which, in itself, is presumably a strong enough base to act as a polymerization initiator for the DCA as it is generated. The only thing obtained was a dark brown product in poor yield. There was no isolatable DCA and the brown material was not characterized.

One other approach of a similar nature was explored in some detail, viz., the use of acetylene Grignards plus cyanogen bromide. Again the expected DCA was not obtained, and after a brief attempt at repeating the reaction, with similar results, this method was not followed up further. The allotted time for the program prevented further excursions into studying other synthetic methods and necessitated our emphasizing the Moureu and Bongrand method. This meant preparing many small batches in ampouls and using them as needed.

4.2 Polymerization Studies

Although the preparation and reactions of dicyanoacetylene had been detailed in the literature (References 1, 3, and 8), prior to the work of Benes, et al, (Reference 2) nothing was mentioned regarding its polymerization behavior. Before DCA was used, other acetylenic compounds, of a hydrocarbon nature, had been investigated regarding their polymerizability (References 9-12). Benes and coworkers were interested in compounds having electron-withdrawing as well as electron-donating groups and they decided upon dicyanoacetylene and acetylenic ethers for their program (Reference 2). Since their reported work, there has been nothing further written about DCA polymerization studies. Based upon discussions with Dr. Rembaum of JPL, it was decided we would explore the copolymerization behavior of DCA via whatever means proved feasible.

Our decision was to first use DCA in a copolymer with styrene. This was based upon the fact that should a true copolymer be obtained, one

could study its behavior via its absorption spectrum. Thus, in analogy to the results obtained with tetracyanoethylene, TCNE, and aromatic molecules in forming charge-transfer complexes, where the absorption spectra show the presence of these complexes (Reference 13), it was believed that a copolymer of DCA with styrene might develop an internal complex and that the presence of the complex might be determined by its absorption spectrum. In addition, solubility characteristics of the homopolymers of DCA and styrene versus those of the copolymer would enable one to see differences in behavior and would be helpful in the characterization of the product.

Anionic polymerization of DCA in toluene solution with n-butyl lithium as initiator was so rapid that the initiator was used up almost immediately upon contact with the large excess of monomer. Furthermore, the heterogeneity of the system (in toluene) removed the active growing polymer and from any other monomer which had not had a chance to react, thereby presumably lowering the degree of polymerization. This, in effect, would also have a tendency to lower the overall rate of polymerization, even though the initial rate might be high. Presumably, this would also affect the copolymerization behavior, as well. It is interesting to note that large amounts of anionic initiator have been required by others even in such solvents as THF or petroleum ether, thereby necessitating the use of a stepwise addition technique for the initiator (Reference 14).

Anionic copolymerizations of DCA with other monomers have not been explored in detail. As our first approach to the problem we believed it might be possible to effect a copolymerization which would not consist of long blocks of DCA followed by styrene blocks. DCA, as with methacrylonitrile, acrylonitrile, methylmethacrylate, etc., is a rapid polymerizer under anionic conditions. Styrene, just as with other aromatic substances (benzene, toluene, naphthalene, etc.), undergoes reactions with electrophilic rather than nucleophilic substances. This means it will tend to repel nucleophilic substances, such as anions, thereby slowing down its tendency to polymerize under anionic conditions. This we have observed in the attempted homopolymerization of styrene in toluene with n-butyl lithium as initiator. After about 21 hours, a very low conversion to polymer was obtained. (See also, Reference 15.) Thus, attempting to take advantage of these facts, we tried a copolymerization of DCA with styrene under anionic conditions in toluene by means of a stepwise addition

of the DCA (the fast polymerizer) to the butyllithium initiated solution of styrene (the slow polymerizer). Due to insolubilization in toluene, the rate of conversion was low.

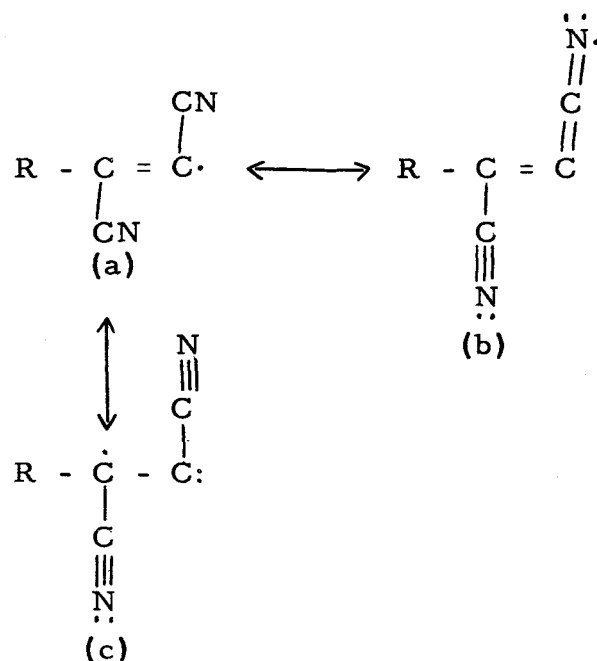
In view of the difficulties encountered with the anionic copolymerization system, we decided to attempt a free radical copolymerization. Here, certain factors would be operable which would enable us to obtain a truer copolymer than could be possible in the anionic system. Thus, in the formation of a radical-initiated copolymer, the following would influence the course of the reaction (Reference 16):

- a. The double bond polarity of the monomers involved
- b. Steric hindrance
- c. The relative energy or reactivity of the radicals generated from each monomer.

Furthermore, for acetylene, the addition reactions resemble those of ethylene, since the two pi-bonds in acetylene are perpendicular to each other and are electronically independent. This, in conjunction with the added fact that the energy required to break one pi-bond in an acetylene is less than that required to break the pi-bond in ethylene (Reference 17), would all have considerable bearing on the polymerizability of DCA. Considering the aforementioned factors, one suspects that DCA might lend itself admirably to copolymerization. For example, it is highly electronegative, therefore capable of combining readily with a generated radical of the proper polarity (styrene is nucleophilic). Also, DCA is a linear molecule (Reference 18) and sterically unhindered. Thus, since the approach of a radical to a double bond is in the plane perpendicular to the atoms attached to the double bond (Reference 19), the polarity, electronic, and steric factors should allow for facile reaction between a generated radical and DCA. In addition, styrene being a monomer having a driving force to form a styrene radical which can resonance - stabilize itself, the probability would exist that the styrene radical would be generated first and it would tend to react preferentially with the electronegative DCA monomer. This would be analogous to the situation between styrene and maleic anhydride, where the planar maleic anhydride being somewhat sterically unhindered, and with electron-withdrawing carbonyl groups to make it electronegative, would react readily with the styrene radical which is somewhat "nucleophilic" by nature.

DCA was homopolymerized and copolymerized with styrene both in solution and in bulk using azo-bis-isobutyronitrile as an initiator. In the first attempts, toluene was used as a solvent. It was anticipated that formation of a copolymer with styrene would mean increased solubility in aromatic solvents, as compared to the solubility characteristics of the DCA homopolymer. The resulting copolymer was not readily soluble in toluene. We obtained a dark brown solution plus a large amount of dark brown solid deposited on the walls of the tube. Subsequently, we used THF as a polymerization solvent since it solubilized everything in our system.

In Table I, we observe the effect that the solvent and monomer have on the rate of total polymer formation. The results shown in Table I are for total recovered polymer - both soluble and insoluble. It is interesting to note that bulk polymerization of DCA is extremely slow whereas in THF it is somewhat more rapid as indicated by the degree of conversion. Furthermore, the violence of the bulk polymerization when styrene is present is also interesting. Thus, if one utilizes the fact that the styrene is the more active monomer to a radical present in the system, it will form the resonance-stabilized styrene radical first. Then, DCA being very electronegative will pick up the styrene radical more readily than a styrene monomer. The next step is possibly more open to question. Looking at the case of the copolymerization of styrene with vinyl acetate, where we have a possibility for resonance stabilization in styrene and much less so far for vinyl acetate, we may try to draw some analogies. Styrene being a reactive monomer due to its conjugation will form a radical readily; vinyl acetate lacking conjugation will not form a radical readily and is considered an unreactive monomer. However, the styrene radical, when once formed, is stabilized by resonance and is relatively unreactive, while the vinyl acetate radical, after it is generated, is not stabilized by resonance and will react rapidly with any monomer near it. The evidence available in the literature shows the vinyl acetate radical to be about a thousand times more reactive than the styrene radical (Reference 20). Now then, considering the fact that the DCA radical has limited resonance-stabilization, as shown on the following page:



where (b) is the most likely form and (c) highly unlikely, we have a radical at the end of a growing polymer chain which should be quite reactive. Thus, by analogy, we could have the following: styrene monomer will pick up an active radical to form a stable styrene radical, and when approached by an electronegative but unreactive monomer (DCA) (analogous to maleic anhydride), it will react readily to hook a DCA unit to the end of the chain, thereby creating a highly active radical which will react rapidly with any monomer near it (analogous to vinyl acetate).

Since DCA does not readily homopolymerize, as shown in Table I, it would probably react preferentially with a styrene monomer. However, other available evidence indicates this may not be the case. For example, dicyanodiacetylene, $\text{N} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv \text{N}$, is a highly conjugated system which is colorless (Reference 21), whereas the polymer we obtain is dark colored, indicating a longer conjugated system. Furthermore, to point up the effect of conjugation on color, we may refer to the well-known example of the effect of conjugation on the diphenylpolyenes, $\text{C}_6\text{H}_5 (\text{CH}=\text{CH})_n - \text{C}_6\text{H}_5$, where n was varied from one to seven; as n increased so did the conjugation. The positions of the absorption maxima also went from the shorter to the longer wavelengths with the increase in conjugation (Reference 22). Thus, arguing by analogy again, one may claim that our copolymer probably has a few DCA units

TABLE I

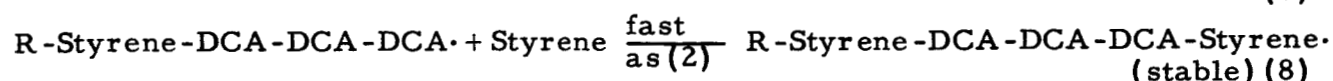
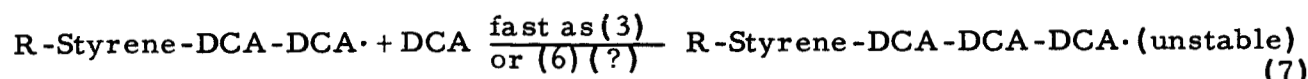
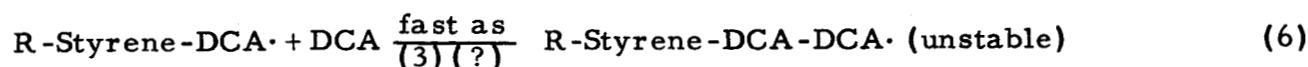
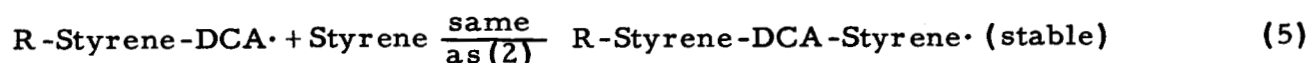
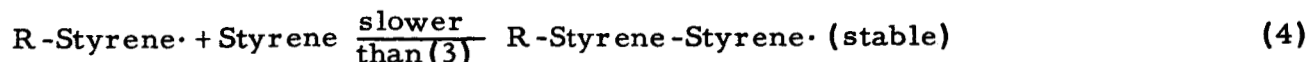
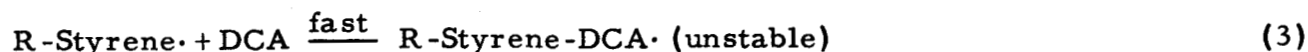
SOLVENT AND MONOMER EFFECTS ON RATE
OF TOTAL POLYMER FORMATION AT 55°C

Run	Monomers (in mls.)	Solvent (in mls.)	Time (hrs)	Catalyst ⁽¹⁾ (g)	Pressure ⁽²⁾ In Tube (mm Hg)	Yield	Remarks
1	DCA (2.6) Styrene (2.8)	Toluene (5.0)	17.5	0.025	8×10^{-5}	4.49 g. (92%)	Pasty black material
2	DCA (3) Styrene (3)	THF (6)	21	0.031	9×10^{-5}	5.27 g. (97%)	Dark gray powder
3	DCA (2)	THF (2.5)	23	0.012	1×10^{-5}	0.8522 g.	Viscous brown material
4	DCA (3.5) Styrene (3.5)	THF (5)	16	0.031	1×10^{-5}	5.442 g. (85%)	Black material
5	DCA (2) Styrene (2)	Acetone (6)	23	0.032	1×10^{-5}	2.8835 g. (80%)	Slightly sticky brown material
6	DCA (1.5)	None	18	0.018	1×10^{-5}	--	Hardly any noticeable amount of polymer formed
7	DCA (3) Styrene (3)	None	0.75	0.031	1×10^{-5}	--	Exploded
8	DCA (3) Styrene (3)	None	0.25	0.031	1×10^{-5}	--	Exploded
9	DCA (2.5) Styrene (2.5)	None	0.75	0.041	1×10^{-5}	--	Exploded
10	DCA (2.6)	None	1397	0.041	1×10^{-5}	0.1728 g.	Dark brown solid, insoluble in H ₂ O, soluble in methanol

(1) Catalyst used was Azo-bis-isobutyronitrile.

(2) Sealed tube polymerizations.

contiguously arranged with styrene being added periodically. Therefore, we can show the sequence of reactions, as follows:



The evidence for the above sequences lies in the following facts:

- a. The polymer is dark colored indicating a reasonably long degree of conjugation as would be obtained from (8) above.
- b. The DCA homopolymerizes in bulk at a very slow rate, but in the presence of styrene copolymerizes explosively. This shows the necessity for having a stable but active radical as from (2) above.
- c. The solubility characteristics, shown in Table II, indicate the presence of a material other than straight polyDCA.
- d. The large electronegativity of DCA would argue for (3) above.
- e. The low degree of resonance-stabilization of the radical would argue for (5), (6), (7), or (8) occurring.

These facts all tend to explain the type of polymer which is obtained.

However, one other thing should be borne in mind: the attempted calculation of the r_1 and r_2 values by means of infrared absorption studies of the copolymer, as performed by Dr. A. Rembaum and Mr. A. Henry at JPL, verifies the fact, as observed by us, that DCA does not homopolymerize readily and presumably has an r_2 very close to zero; while the styrene r_1 value is 1.40.

TABLE II
EXTRACTION OF DCA/STYRENE (1:1) COPOLYMER

Time	Solvent	Weight of Sample Collected, in Grams, After Removal of Solvent	Remarks
17 hrs 30 min	H ₂ O	0.34619	Clear, dark brown solution when hot but cloudy when cool.
7 hrs 10 min	H ₂ O	0.04925	
16 hrs 15 min	H ₂ O	0.08685	
7 hrs 15 min	H ₂ O	0.0421	
Total 48 hrs 10 min		0.5244	
16 hrs 25 min	MeOH	1.34805	A dark brown, slightly turbid solu- tion when hot but very muddy looking when cool.
7 hrs 20 min	MeOH	0.7250	
15 hrs 40 min	MeOH	0.28386	
8 hrs 15 min	MeOH	0.1526	
Total 47 hrs 40 min		2.50951	
3 hrs 45 min	Toluene	0.16182	A seemingly clear light brown (possibly colloidal) solution when hot but with some particles set- tling out when cool.
17 hrs	Toluene	0.3447	
6 hrs 40 min	Toluene	0.04525	
15 hrs 40 min	Toluene	0.0670	
Total 43 hrs 5 min		0.61877	
21 hrs	Acetone	0.11328	Clear brown solution.
Total 159 hrs 55 min		3.76596	

Starting sample weight: 3.7728 g.

Recovered weight: 3.7660 g.

Loss in weight: 0.0068 g.

This means that to explain the formation of the dark color in the polymers and the low molecular weights obtained, one must assume that the DCA radical adds to a DCA monomer at least once or twice and then the chain terminates, or adds styrene before terminating. Disproportionation would not be possible with a DCA radical at the end and styrene is known to terminate by coupling. Although we were unable to obtain good, reproducible molecular weight data, our spread was in the 200-400 region, and this, in conjunction with the color and rates of polymerization, would argue for the fact that in the aforementioned sequence of reactions, (2) followed by (3) then (6) and termination by coupling would be the most likely explanation of all the observed facts.

Table III shows the rate of conversion to polymer for varying volume ratios of DCA and styrene. The most interesting aspect of this table is the softening point data of the copolymers. In Table IV we have the data showing the chemical analysis for low conversion polymer. This information was to have been used for the determination of the r_1 and r_2 ratios but the carbon, hydrogen and nitrogen analyses were somewhat questionable and non-reproducible thereby causing us to rely more on the infrared spectra results for the percent styrene in the copolymer, as shown in Table V. It is interesting to note in Table V that the percent styrene found for a 50-50 (volume basis) copolymer, where the polymerization time was varied from two to 21 hours, averaged to a value close to that for a similar mixture in another two hour run, viz., 76% average for runs 1-4 versus 73% for run 6. The styrene content appeared to remain essentially constant throughout runs 1-4, so that the copolymer composition is the same at high conversion as it is at low conversion.

The result obtained by Mr. A. Henry at JPL for the conductivity of a free-radical initiated DCA polymer was not much better than that obtained previously by Dr. A. Rembaum of UPL for an anionic initiated polymer. In the present run, a value of less than 10^{-13} mho-cm⁻¹ was obtained. This result is in question as it appeared to be just beyond the limit of the sensitivity of the 610A Keithley Electrometer being used for the measurement. The value found by Benes, et al, for the anionic-initiated polymer was 10^{-9} to 10^{-12} mho-cm⁻¹ as measured in pressed disks between Pt electrodes under pressure in high vacuum (Reference 14).

TABLE III

RATE OF CONVERSION AND SOFTENING POINT OF COPOLYMERS⁽⁸⁾A. 50/50 DCA/Styrene (Volume Basis)

	2 hrs	4 hrs 10 min	6 hrs	21 hrs
Monomers	DCA (1.7 ml) Styrene (1.7 ml)	DCA (1.6 ml) Styrene (1.6 ml)	DCA (2.7 ml) Styrene (2.7 ml)	DCA (1.6 ml) Styrene (1.6 ml)
Solvent (THF)	4.0 ml	4.0 ml	5.2 ml	4.0 ml
Catalyst ⁽¹⁾	0.02 g.	0.022 g.	0.03 g.	0.02 g.
Yield	0.4927 g. (16.1%) (4)	0.8575 g. (29.8%) (4)	2.689 g. (58.6%) (4)	2.5478 g. (88.5%) (4)
Softening Point ⁽²⁾	92°C ⁽³⁾	97°C ⁽³⁾	115°C ⁽³⁾	113°C ⁽³⁾

B. 25/75 DCA/Styrene (Volume Basis)

Monomers	DCA (1.8 ml) Styrene (5.4 ml)	DCA (1.9 ml) Styrene (5.7 ml)	DCA (1.7 ml) Styrene (5.1 ml)	DCA (1.6 ml) Styrene (4.8 ml)
Solvent (THF)	7.2 ml	7.6 ml	6.8 ml	6.4 ml
Catalyst ⁽¹⁾	0.041 g.	0.042 g.	0.04 g.	0.041 g.
Yield	0.7122 g. (11%)	1.8020 g. (26.4%)	2.2733 g. (37.1%)	3.841 g. (66.6%)
Softening Point ⁽²⁾	47°C ⁽³⁾	53°C ⁽³⁾	72°C ⁽³⁾	57°C ^(3,5)

TABLE III (CONT'D)

RATE OF CONVERSION AND SOFTENING POINT OF COPOLYMERS⁽⁸⁾C. 75/25 DCA/Styrene (Volume Basis)

	2 hrs	4-1/4 hrs	5-3/4 hrs	21 hrs
Monomers	DCA (1.7 ml) Styrene (0.57 ml)	DCA (1.7 ml) Styrene (0.57 ml)	DCA (1.7 ml) Styrene (0.57 ml)	DCA (1.7 ml) Styrene (0.57 ml)
Solvent (THF)	2.3 ml	2.3 ml	2.3 ml	2.3 ml
Catalyst ⁽¹⁾	0.019 g.	0.016 g.	0.017 g.	0.015 g.
Yield	0.2390 g. (11.7%)	0.6882 g. (33.7%)	0.6894 g. (33.8%)	1.2453 g. (61.0%)
Softening Point ⁽²⁾	125°C ⁽⁶⁾	127°C ⁽³⁾	105°C ⁽⁶⁾	130°C ⁽⁶⁾

D. 100 DCA

	1397 hrs
Monomer	DCA (2.6 ml)
Solvent	None
Catalyst ⁽¹⁾	0.041 g.
Yield	0.1728 g. (7%)
Softening Point ⁽²⁾	160°C ⁽⁷⁾

(1) Catalyst was Azo-bis-isobutyronitrile.

(2) Fisher-Johns Melting Point Apparatus used.

(3) The softening point was followed beyond softening range. Physical changes were noted as the temperature rose above the softening point. At about 150°C the melt turned a darker shade of brown, at 200°C the liquid began to bubble, at 300°C the liquid slowly began to turn darker and harden to a brownish-black solid insoluble in H₂O, hexane or THF.

- (4) Percent yield is based on an approximate density of 0.9 for both styrene and DCA.
- (5) Odor of benzaldehyde when cover glass was removed from over sample after heating.
- (6) Changes were similar to (3) above except that hardening to a black solid was observed at 280°C.
- (7) Seemed to lose edge sharpness but did not melt to a liquid as others did. As temperature rose, color became deep black but sample did not seem to diminish appreciably in size. In fact, it seemed to resolidify after initial softening.
- (8) Polymerized in sealed tubes at 55°C.

TABLE IV

LOW CONVERSION POLYMERIZATIONS AT DIFFERENT MONOMER RATIOS

Monomer Ratios (Volume Basis) DCA/Styrene	Monomers (in mls.)	Solvent ⁽²⁾ (in mls.)	Time (hrs)	Catalyst ⁽¹⁾ (g.)	Yield	Softening ⁽³⁾ Point	Chemical Analyses
10/90	1.23 DCA 11.7 Styrene	12.0	2	0.049	0.104 g. (8.9%)	160°C	
20/80	1.65 DCA 6.6 Styrene	8.0	2	0.049	0.348 g. (4.7%)	137°C	
25/75	1.75 DCA 5.25 Styrene	6.25	2	0.025	0.373 g. (5.9%)	150°C	
40/60	1.6 DCA 2.4 Styrene	4.25	2	0.025	0.440 g. (12.2%)	122°C	Carbon-75.42% Hydrogen-4.00% Nitrogen- (18.67%) (18.93%)
50/50	1.7 DCA 1.7 Styrene	3.4	2	0.016	0.377 g. (12.3%)	130°C	Carbon-75.79% Hydrogen-4.13% Nitrogen-18.65%
60/40	1.7 DCA 1.1 Styrene	2.8	2	0.014	0.254 g. (12.7%)	102°C	
75/25	2.65 DCA 0.90 Styrene	3.5	2-1/6	0.02	0.406 g. (12.8%)	90°C	Carbon- (75.51) (75.68) Hydrogen- (4.37) (4.43) Nitrogen- (17.11) (18.37)

TABLE IV (CONT'D)

LOW CONVERSION POLYMERIZATIONS AT DIFFERENT MONOMER RATIOS

Monomer Ratios (Volume Basis) DCA/Styrene	Monomers (in mls.)	Solvent ⁽²⁾ (in mls.)	Time (hrs)	Catalyst ⁽¹⁾ (g.)	Yield	Softening ⁽³⁾ Point	Chemical Analyses
80/20	2.5 DCA 0.5 Styrene	3.0	3	0.015	0.350 g. (12.5%)	116°C	Carbon- (74.58) (74.59) Hydrogen- (3.90) (3.96) Nitrogen- (18.72) (17.98)
90/10	2.8 DCA 0.3 Styrene	3.0	4	0.014	0.218 g. (7.8%)	150°C	Carbon-74.14% Hydrogen-3.89% Nitrogen-18.10%

(1) Azo-bis-isobutyronitrile

(2) Tetrahydrofuran

(3) Softening but not liquification

TABLE V
PERCENT STYRENE IN POLYMER
VERSUS STARTING MONOMER MIXTURE

Run	Monomer Ratios (Volume Basis) DCA/Styrene	Time (hrs)	Percent ⁽¹⁾ Styrene
1	50/50	2	79
2	50/50	4	71
3	50/50	6	80
4	50/50	21	75
5	40/60	2	55
6	50/50	2	73
7	75/25	2	80
8	80/20	2	86
9	90/10	2	91

(1) Determined by means of infrared spectroscopy.

5.0 CONCLUSIONS AND RECOMMENDATIONS

In order to obtain a material from polyDCA capable of acting as a semiconductor, we must understand the mechanism of conduction in polyDCA. This necessitates investigating a number of dependent problems; namely, better ways of obtaining dicyanoacetylene monomer in large yield, the polymerization characteristics of DCA, and ultimately the preparation of polymers and copolymers capable of acting as semiconductors either intrinsically or as charge-transfer complexes.

Although difficulties were encountered in the preparation and polymerization of DCA, it is still a potentially interesting monomer for further work. Our results show it can be prepared readily from acetylenedicarboxylic acid dimethyl ester in fair yield. By developing a better reaction flask, it is believed this yield can be increased. The most important part of this approach is to get the monomer out of the reaction zone as quickly as possible. To do this one has to prevent the solid phase reaction from caking up. It may be that an indented Morton flask may prove useful. However, other synthetic routes may also prove feasible. Thus, instead of the lithium acetylide, one may want to use a copper acetylide with cyanogen bromide. The copper compound may be less active as a polymerization initiator. Still other routes are also possible. For example, dehydrohalogenations of a dihalosuccinonitrile or dehalogenation of a tetrahalosuccinonitrile are other possibilities. Suffice-it-to-say, the utilization of DCA will be greatly increased if it were more readily available. Some effort should be devoted toward this goal.

The polymerization reaction of DCA has been barely explored. Aside from the work of Benes, et al, (References 2 and 14), and an attempted polymerization at the Jet Propulsion Laboratories by Dr. A. Rembaum, we are the only others presently reporting on this reaction. Our initial attempts with regard to the radical polymerization have been sketchy and incomplete. Due to the time limitations, we have restricted ourselves to only styrene as comonomer, and only to attempting to obtain the rate of polymerization. The data was too limited to enable us to calculate reactivity ratios. However, from the few analytical results shown in Table IV, as questionable as they might be, we seem to find some corroboration of the calculated values of r_1 and r_2 as determined by infrared spectroscopy. Taking averages of the doubtful nitrogen

values, we note that there is a decreasing amount of nitrogen in the polymer with increasing dicyanoacetylene in the original feed. It is obvious that further work is necessary to refine the results to where a good calculated value for the r_1 and r_2 could be obtained. However, our present approximation appears in good agreement with the experimental results and warrants further effort towards determining more accurate values. Another possible approach would be to use higher temperatures for the polymerization. Increasing the temperature would increase the reactivity and subsequently the rate. This may change the reactivity ratios, as well.

A program of particular consequence is that directed towards understanding the mechanism of conduction in polyDCA. Benes, et al (Reference 14) showed conductivities in the order of 10^{-9} to 10^{-12} mho-cm⁻¹. This is considerably higher than the values obtained at JPL for either the anionic or free radical initiated systems. Their results were in the region of 10^{-13} mho-cm⁻¹ and are questionable due to the fact that they were at the limit of the sensitivity of their instrument. Obviously, one would like to know how to get better values. It may be that our polymer structure is not what we claim it to be. We do not know whether branching has occurred and if so, to what extent this would interfere with conduction. In addition, the question of oxidation from molecular oxygen is probably a consideration. This has been implied by Benes to Dr. Rembaum. It becomes quite obvious, therefore, that we know comparatively little about the polymerizability of DCA and the structure of the polymer. Thus, much further work is warranted in obtaining a polymer of DCA of reasonably high molecular weight, studying the properties of the polymer and copolymers (using styrene, acrylates, dienes, etc.), and determining the effect that oxygen, metal electrodes and their contact points, and physical form, i. e., film, pressed disc, etc., have on the conductivity. Although the conductivities reported, to date, have not been appreciable, the possibility of developing polymeric charge-transfer complexes are potentially great with polydicyanoacetylene. This polymer is probably one of the best electronegative materials available at the present and lends itself admirably to complexes with electron-donating materials. This has not been explored, as yet. It can be readily seen, therefore, that many areas remain open for further investigation before one can write polyDCA off as a poor example of a conducting material.

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